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Solvent extraction of fish oil.

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SOLVENT EXTRACTION OF FISH OIL

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ABSTRACT

An attempt was made to separate raw fish oil into two fractions of different degrees of unsaturation by solvent extraction. The mixed solvents tried were (1) methanol-furfural, (2) methanol-methyl ethyl ketone, (3) methanol-ethylene dichloride, (4) methanol-nitroethane, and (5) methanol-n-hexane. Removal of solvent from the extracted fish oil was very difficult. A special stripping column was constructed to assist in this operation.

Improved iodine numbers were obtained only on the methanol-ethylene dichloride-fish oil system at room temperature. However drying tests were favorable upon fish oil, extracted at 6°C with methanol-n-hexane.

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INTRODUCTION

The work reported in this thesis, "Solvent Extraction of Fish Oil", was undertaken in the hope that the drying properties of fish oil might be improved. It was hoped that the color and odor of the oil might also be improved.

Fish oil is a complex mixture of organic compounds. The principle components are mixed triglycerides of both saturated and unsaturated fatty acids. Since the rate of drying of an oil is a function of the degree of saturation, it would be desirable to separate the saturated and unsaturated compounds. Solvent extraction shows promise for selective separation of these fatty acids.

The work of Zabban and Talbott (24) indicates that solvent removal from the oil is a major problem. They used furfural as a solvent for fish oil but were unable to remove sufficient quantities of furfural from either the extract or raffinate to obtain comparative results.

A number of men have worked with single solvent systems and have published papers and obtained patents on their results. Most of the organic solvents which show high selectivity for unsaturated fatty acids at very low temperatures are completely miscible with fish oil at room temperature. Methanol exhibits a slight selectivity for unsaturated triglycerides and is but slightly miscible with fish oil at room temperatures. Therefore, it was decided to use binary solvents in this work to obtain a separation of saturated and unsaturated glycerides at higher temperatures than would otherwise be possible.

The fish oil was that of "Brevoortia-tyrannus" (menhaden). The crude oil varies in composition from barrel to barrel. The solvents used were technical grade.

HISTORICAL

A large number of methods have been proposed for determining iodine numbers. Govindarajan (12) has shown that the methods of Rosemund-Kuhnhenn, Kaufmann, and Hanus give comparable results, while the iodine numbers obtained by the Wiis method tend to run high. Montequi and Doadrio (16) found that the Hanus and the Kaufmann methods for determining iodine numbers were the most generally useful. Lo and Chu (14) found, upon comparison of the Hanus, Wiis, and Hubl methods, that the Hanus method gave the most satisfactory results.

Much work has been done on solvent extraction of vegetable oils, but very little work has been done on marine oils. The references, which follow, indicate the magnitude and direction of research in the field of solvent extraction of oils. References have been included on fractional crystallization of oils in the presence of a selective solvent.

Zabban and Talbott (24) have worked on extracting fish oil with furfural without much success. Ruthruff and Wilcock (21) described a process for extracting soybean oil with furfural to obtain a highly unsaturated constituent, which in turn, was extracted with V M & P naphtha to remove materials which retard drying by acting as antioxidants. Freeman (9) was granted a patent for separation of saturated and unsaturated fractions of vegetable oils with furfural or furfuryl alcohol as a selective solvent. Jenkins (13) also obtained a patent utilizing a furan compound for separation of saturated and unsaturated compounds in vegetable oils.

Polland, Vix and Gastrock (19) used hexane to extract oil from cottonseed and peanut meal. Patents were issued to Freeman (8) on processes for selectively separating mixed glycerides. The material is brought into contact with an organic polar solvent at a low temperature. Under these conditions the solvent is relatively insoluble with the saturated glycerides. Forman and Brown (6) investigated the solubility of fatty acids as temperatures down to -50°C in acetone, methanol and Skelly Solve B. Their results indicate effective separation. Baldwin and Park (2) have successfully crystallized out the more saturated glycerides of destearinated menhaden oil from an acetone solution at low temperatures, leaving an oil with a high iodine number. At - 60°C 87.4% of the oil had precipitated. The filtrate still contained 12.6% of glycerides having an iodine of 264.2. The iodine number obtainable by crystallization from acetone at -15°C was 179.0. Bull and Wheeler (5) studied the separation of soybean oil by crystallization from acetone at temperatures of -15°C to - 76°C. Crystallization from higher solvent ratios at correspondingly lower temperatures gave the most efficient separation with regard to iodine number for a given yield.

THEORETICAL

A number of characteristics must be considered in chosing a solvent or solvent system. Gard and Ragatz (10) have listed nine factors to be desired in a good solvent.

1. High efficiency and selectivity for the quality of product desired.
2. High degree of stability under handling and operating conditions.
3. Ready gravity separation of its extract and raffinate phases.
4. Residual traces left in the oil should have no deleterious effect on the oil's characteristics.
5. Should be recoverable from the extract and raffinate oils.
6. Should be non-corrosive.
7. Should be non-toxic.
8. Should be fluid at atmospheric conditions.
9. Should be inexpensive.

Goss (11) has added that in vegetable oil extraction

1. The solvent must be recovered without raising the temperature above a rather indefinitely defined maximum.
2. Equipment fabrication must be free of tendencies to contaminate the oils, e.g., a minute amount of copper is fatal to the stability of soybean oil.

In a ternary system consisting of two immiscible or slightly miscible liquids and a third liquid, miscible in each of the other two, a two phase liquid system will exist. The mutually miscible liquid, or consolute, will distribute itself between the two phases in accordance with the distribution law:

$$y = K^1 x$$

where y = solute concentration in one liquid (extract) phase.

x = solute concentration in the other liquid (raffinate) phase.

K^1 = the "distribution coefficient".

For most systems the value of K^1 varies considerably with concentration (20). Temperature variations also effect the value of K^1.

The plotting on triangular graph paper, of the compositions of the equilibrium phases over a range of total compositions, holding the temperature and pressure constant, will result in a unique curve. Since, at equilibrium conditions, each phase is mutually saturated, this curve is actually a solubility curve. Therefore the area beneath the mutual solubility curve represent s a two phase region; while the area outside represents a single phase region.

A point exists on the mutual solubility curve where both phases have the same composition and density (18). This point is termed the "plait point" or "critical point". The "plait point" is not necessarily at the maximum of the isotherm.

In fact, it is usually displaced from the apex of the isotherm because the mutual solubility curve is seldom symmetrical. However the plait point is located where the radius of curvature of the curve has reached a temporary maximum (18).

A straight line connecting points on the mutual solubility curve, representing coexisting equilibrium phases, is called a tie-line (18). All compositions represented by points on the same tie-line will separate into the same two phases, differing only in the relative amounts of the two layers. Since the plait point is usually displaced from the maximum of the isotherm, the tie-lines are usually not parallel to the base of the triangular diagrams.

If the weight percentages of the two non-consolute liquids are plotted on rectangular coordinates, the binodal curve approximates a regular hyperbola (3). Branckner et.al. also showed that a smooth tie-line curve can be constructed by proper plotting. This curve will intersect the equilibrium curve at the "plait point" and is formed by plotting the weight percentage of the first nonconsolute constituent in one liquid phase against the weight percentage of the second non-consolute constituent in the other equilibrium liquid phase. Bachman (1) has shown that the above mentioned tie-line curve can be reduced to a straight line by plotting the weight percent "A" in the A-rich layer against the ratio of the weight percent "A" in the A-rich layer to the weight percent "B" in the B-rich layer. "A" and "B" are the nonconsolute components.

Othmer and Tobias (17) introduced a modification for highly immiscible conconsolute components, which yields a straight tie-line curve of unit slope. This simplification of Bachman's plots does not hold for partially miscible non-consolutes.

As is true with most states of equilibria, temperature is a variable of great importance in a ternary liquid equilibrium. Briggs and Comings (4) have studied the effect of temperature on liquid-liquid equilibrium. They discovered that the effect of temperature variations can not be predicted without the plotting of data. The solubility curve may or may not be effected appreciably and the slope of the tie lines may or may not be altered a great deal, dependent upon the system under consideration.

Quaternary solvent systems may be represented by three dimensional space diagrams. Randall and Longtin (20) have presented a simplified, unique method of representing quaternary systems on a two dimensional plot (15). Much work needs to be done on theoretical considerations of quaternary solvent systems.

Fish oil can be considered as consisting of two miscible components, triglycerides of unsaturated fatty acids and triglycerides of saturated fatty acids. Although each fatty acid differs in its solubility characteristics, and although each triglyceride may contain any of these fatty acid radicals; it is believed that the above simplification is reasonable.

The validity of this assumption is strengthened by observing that the differences in the solubility characteristics of the various individual fatty acids and of the individual unsaturated acids are negligible when compared with the differences in the solubility characteristics between the corresponding members of the two groups. Even though all three fatty acid chains of the single triglyceride may be different, at least two of them will be either saturated or unsaturated. Therefore the molecule will tend to act as though it were either saturated or unsaturated.

If the fish oil is considered as the solute, the more miscible of two solvents as the diluent and other solvent as the solvent, ternary diagrams may be constructed and the theory presented in the first part of this section may be applied. It must be borne in mind, however, that such a ternary system is only an approximation of the condition existing. The quaternary system obtained by considering the oil as two components, as noted in the previous paragraph, approaches the true condition of state much more closely. Therefore, it is to be expected that ternary experimental data will deviate somewhat from the theoretical.

The rates of change in the degree of solubility of various fatty acids in some solvents, with respect to temperature, are considerably different. Therefore, the error introduced by considering the fish oil as a single component is expected to become appreciable as the temperature is decreased very

much below room temperature.

At temperatures near $0^{\circ}C$ the simplification of the mixed solvent-oil system, to allow the use of ternary diagrams, is expected to be impossible. The deviation of experimental from theoretical would be prohibitive. Under these circumstances we must revert to a quaternary system.

APPARATUS AND PROCEDURES

Extractions were made by thoroughly shaking the components in a separatory funnel, and then allowing the phases to separate.

Simple vacuum distillation was used on some samples to attempt to remove the solvent; while some samples were passed through both the vacuum distillation apparatus and a modified falling film evaporator.

The vacuum distillation apparatus (Fig. 1) is operated under a vacuum of approximately 730 mm Hg. This is the maximum vacuum obtainable with the aspirator available. A hot plate "A" is the source of heat and a water bath "B" prevents too rapid a temperature rise. The extract or raffinate is placed in a distilling flask "C". When ebullution occurs, the vapor passes into vapor space "E". Some refluxing occurs at this point due to heat losses, but the primary function of this enlarged section is to prevent entrainment of oil in the solvent vapor. The vapor next passes upward to a total condenser "G" placed between the still and the line to the aspirator "H". The condensate drains downward through trap "F" and into receiver "I". The temperature of the oil can be observed continuously by reading thermometer "D".

It was discovered that the vacuum distillation was insufficient to remove the last traces of solvent, therefore an evaporator was utilized as a subsequent step. Frampton and Giles (7) have described a low pressure extraction apparatus

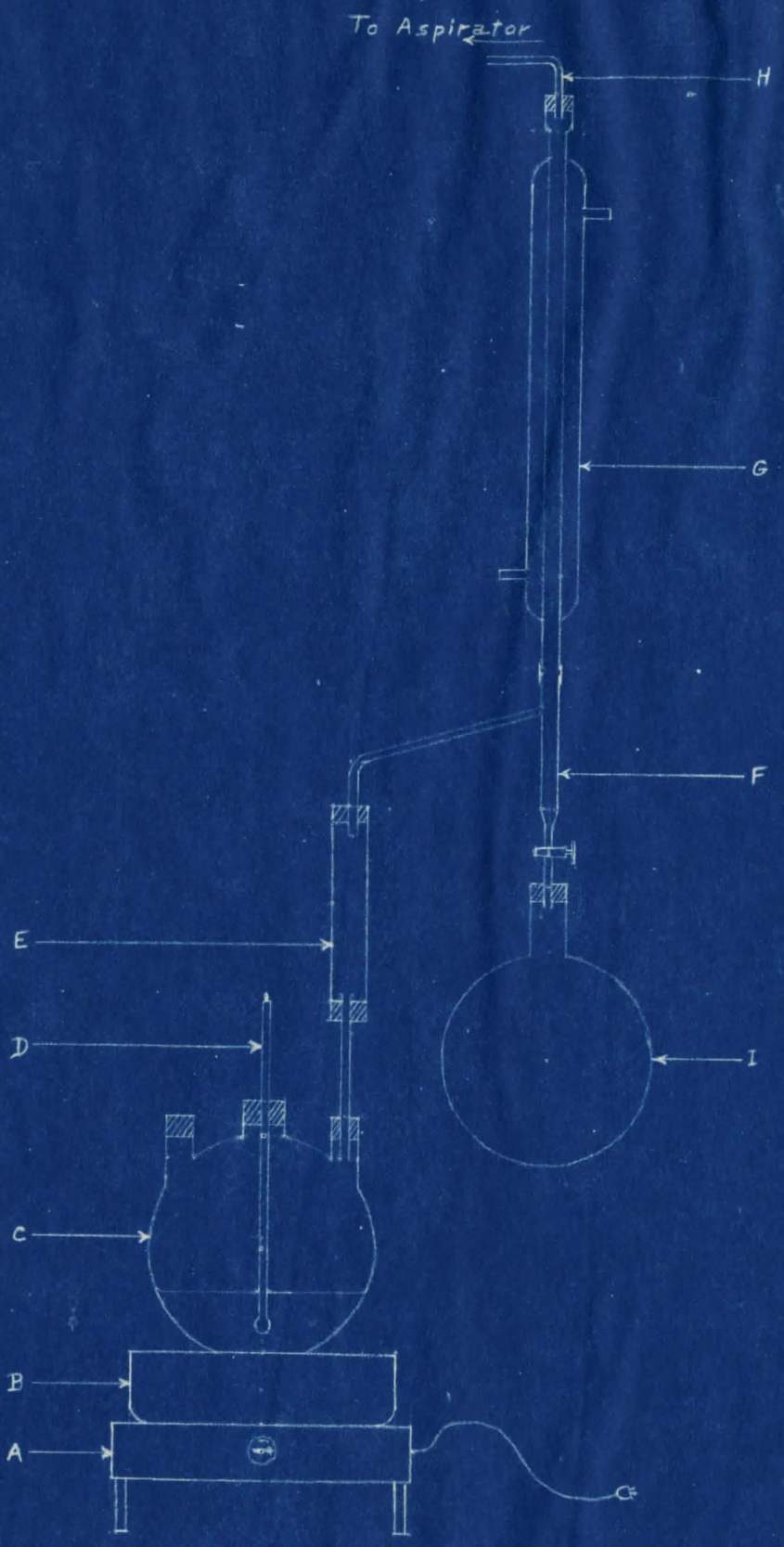

FIG. 1: VACUUM DISTILLATION APPARATUS

for use with cottonseed. They also utilized the same equipment to remove the solvent from the extracted oil. This apparatus would be extremely difficult to construct and would be of limited capacity.

A simplified procedure for the stripping of solvent from heat sensitive oils, such as fish oil, has been devised (Fig.2). The oil-solvent mixture is admitted to a condenser "A" through a separatory funnel "B" and drops into a receiver "C". A low boiling liquid is boiled in boiler "D", the vapor passing upward and entering the jacket of condenser "A" at the top. The liquid that is condensed by the transfer of heat to the descending film of oil mixture in the inner tube, flows down the walls of condenser "A" and back to boiler "D". If the heating system were a completely closed system, the pressure would become excessive. This is prevented by venting the boiler "D" to the atmosphere through condenser "E". This condenser prevents loss of boiler fluid in the system.

Better control of the time that the oil is in contact with the warm surface can be obtained if condenser "A" is the type whose inner tube is in the form of a helix. A third condenser "F" and receiver "G" is inserted between the exhaust line from "A" and the aspirator to recover the solvent.

In these experiments it was found that warm water was a very good heating medium.

All iodine numbers were determined by the Hanus (23) method. A sample (between 0.1 and 0.2 gram) is weighed into

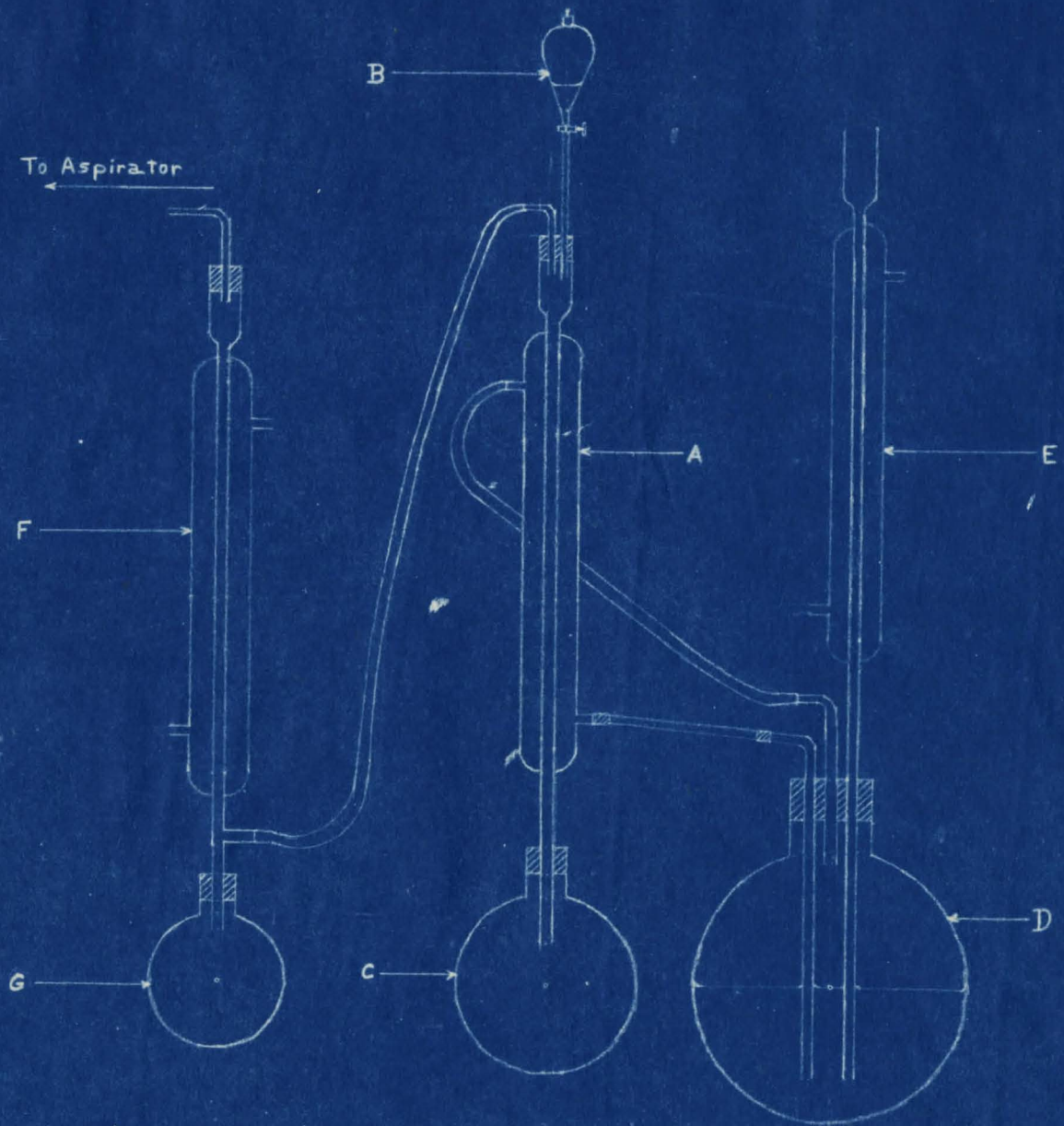

FIG. 2: FALLING-FILM EVAPORATOR

a glass stoppered Erlenmeyer flask and dissolved in ten milliliters of chloroform or carbon tetrachloride. Twenty-five milliliters of Hanus solution* are pipetted into the flask, the contents shaken well, and allowed to stand for exactly thirty minutes with occasional shaking. Approximately one hundred milliliters of water and ten milliliters of potassium iodide are then added to the flask and the mixture is titrated to the starch end-point with 0.1 N sodium thiosulfate. A blank must also be run.

Extractions where volumes of each phase were important, i.e., for equilibrium data, were accomplished by shaking the components in a one hundred milliliter graduate cylinder, allowing the phases to separate, measuring the volumes, and pipetting off samples for density determinations. Densities were determined on a Westphal balance. Equilibrium data were obtained and plotted according to the method of Othmer, White and Trueger (18). Constant temperatures for equilibrium data determinations were maintained by a water bath, to which ice cubes were added whenever needed.

* See Appendix

EXPERIMENTAL

The work of Zabban and Talbott (24) with furfural suggested the possibility of using a methanol-furfural-fish oil system. Both the raffinate and the extract of this system retained a distinct odor of furfural, even after vacuum distillation and passage through the falling film evaporator, described in the preceding section.

The iodine number of the raffinate, as shown in Table I, was approximately equal to that of the raw oil. Extraction of the furfural treated oil with V M & P naphtha to remove antioxidants was unsuccessful. The distillate resulting from vacuum distillation of the extracted oil smelled of furfural, but the residue in the still pot also retained a strong furfural odor.

The system methanol-methyl ethyl ketone-fish oil was given some consideration but the results were unsatisfactory. Very little fish oil was extracted. The extract layer was vacuum distilled until loss in volume made it necessary to stop. The sample still smelled of methyl ethyl ketone. Iodine numbers were determined on the extract resulting from this system. The iodine values obtained were very low.

Methanol-ethylene dichloride was next considered as a potentially successful solvent system. The work of Freeman (8) indicates that the more unsaturated triglycerides should accumulate in the extract layer of the system methanol-ethylene dichloride-fish oil.

TABLE I: IODINE NUMBERS

Sample	Iodine Number	
	(1)	(2)
Raw Oil	166.0	165.0
Furfural treated raffinate	168.8	
Ethylene dichloride-methanol extract	196.3	
$_A$(a)	157.6	157.6
$_B$(b)	150.0	153.0
Raw Oil / nitroethane	27.4	24.9
Methyl ethyl ketone-methanol extract	44.2	46.2

(a) Decanted raffinate of an extraction of methanol-nitroethane-fish oil system in the ratio of 35-15-25.

(b) Raffinate of methanol-nitroethane-fish oil system in the ratio of 45-5-25.

An equilibrium diagram was determined for the system methanol-ethylene dichloride-fish oil, at 60°F, and the results presented in Tables II and III and Fig. 3. These data indicate the possibilities of methanol-ethylene dichloride as a mixed solvent for fish oil extraction.

A solution was prepared consisting of ten milliliters of ethylene dichloride and forty milliliters of methanol. This mixed solvent was used for the extraction of twenty-five milliliters of raw fish oil, and the two phases were allowed to separate. The light phase, or extract, was lemon yellow. The raffinate was cloudy but became clear upon vacuum distillation to 25°C. The extract layer consisted of methanol and ethylene dichloride, saturated with the more unsaturated fraction of the fish oil. The extract was vacuum distilled to approximately one-fifteenth of its original volume. The residue in the still pot separated into two phases. The heavy phase was oily in appearance. Iodine numbers were determined on the oily layer and are given in Table I. Experiments with ethylene dichloride are being conducted by Freeman of Pittsburg Glass Company.

Available literature indicated that the system methanol-nitroethane-fish oil should have possibilities. A number of extractions were made at atmospheric temperature and the results were low. The iodine numbers were somewhat lower than the values for raw oil. Table I shows some values that were obtained.

The comparison of iodine numbers obtained on raw fish oil and those resulting from raw oil containing one drop of nitro-

TABLE II: TIE LINE DATA (METHANOL-ETHYLENE DICHLORIDE-FISH OIL SYSTEM AT 60°F.)

Sample	Overall Composition								
	Methanol			Fish Oil			Ethylene Dichloride		
	ml.	wt.	wt.%	ml.	wt.	wt.%	ml.	wt.	wt.%
1	31	24.378	37.20	31	28.625	43.68	10	12.531	19.12
2	31		35.83	31		42.07	12	15.037	22.10
3	31		34.56	31		40.58	14	17.543	24.87
4	31		33.37	31		39.18	16	20.050	27.45
5	31		32.36	31		37.88	18	22.556	29.85
6	31		31.23	31		36.67	20	25.062	32.10
7	31		30.26	31		35.53	22	27.568	34.22
8	31		29.34	31		34.46	24	30.074	36.20

Sample	Wt. of Raffinate	Wt. of Extract	Wt.of Raffinate/Wt.of Extract
1	37.00	28.66	1.29
2	38.39	29.70	1.29
3	40.50	30.02	1.35
4	43.60	29.49	1.48
5	46.50	29.07	1.60
6	48.72	29.35	1.66
7	50.25	30.30	1.66
8	52.53	30.56	1.72

TABLE III: EQUILIBRIUM DATA ON METHANOL-ETHYLENE DICHLORIDE-FISH OIL SYSTEM

Titration of Oil into Methanol / n-Hexane

ml Me	ml EDC	ml Oil	Wt. MeOH	Wt. EDC	Wt. Oil	% MeOH	% EDC	% Oil
20	2	0.10	15.728	2.5062	0.0925	85.82	13.68	0.5
20	4	0.45	15.728	5.0124	0.4162	74.34	23.69	1.97
20	5	0.60	15.728	6.2655	0.5550	69.75	27.79	2.46
20	6	0.75	15.728	7.5186	0.6938	65.70	31.41	2.90
20	7	0.90	15.728	8.7717	0.8325	62.09	34.63	3.29
20	8	1.00	15.728	10.0248	0.9250	58.96	37.58	3.47
20	9	1.45	15.728	11.2779	1.3412	55.48	39.79	4.73
20	10	2.0	15.728	12.5310	1.8500	52.24	41.62	6.14
20	11	2.4	15.728	13.7841	2.2200	49.56	43.44	7.00
20	12	3.1	15.728	15.0372	2.8675	46.77	44.72	8.53
20	13	3.8	15.728	16.2903	3.5150	44.26	45.85	9.89
20	17	7.5	15.728	21.3027	6.9375	35.77	48.45	15.79
20	---	---	15.728	-------	------	100.00	-----	-----

TABLE III (CONT.): EQUILIBRIUM DATA ON METHANOL-ETHYLENE DICHLORIDE-FISH OIL SYSTEM

Titration of Methanol into Oil / n-Hexane

ml Oil	ml EDC	ml MeOH	Wt. Oil	Wt. EDC	Wt. MeOH	% Oil	% EDC	% MeOH
20.0	2	0.9	18.500	2.5061	0.70776	85.20	11.54	3.26
20.0	4	1.0	18.500	5.0124	0.78640	76.14	20.63	3.24
20.0	8	1.6	18.500	10.0248	1.25824	62.12	34.41	4.22
20.0	10	2.1	18.500	12.5310	1.65144	56.61	38.34	5.05
20.0	12	2.8	18.500	15.0372	2.20192	51.76	42.07	6.16
20.0	13	2.9	18.500	16.2903	2.28056	49.90	43.94	6.15
20.0	14	3.7	18.500	17.5434	2.90968	47.49	45.04	7.47
20.0	16	4.2	18.500	20.0496	3.30288	44.20	47.91	7.89
20.0	18	5.8	18.500	22.5558	4.56112	40.56	49.44	10.00
20.0	20	7.5	18.500	25.0620	5.89800	37.40	50.67	11.92
20.0	22	8.4	18.500	27.5682	6.60576	35.12	52.33	12.54
20.0	24	11.1	18.500	30.0744	8.72904	32.28	52.48	15.23
20.0	26	13.6	18.500	32.5806	10.69504	29.95	52.74	17,31
20.0	27	14.8	18.500	33.8337	11.63872	28.90	52.90	18.19
20.0	29	18.4	18.500	36.3399	14.46976	26.69	52.43	20.88
20.0	---	0.4	18.500		0.31456	98.33	-----	1.67

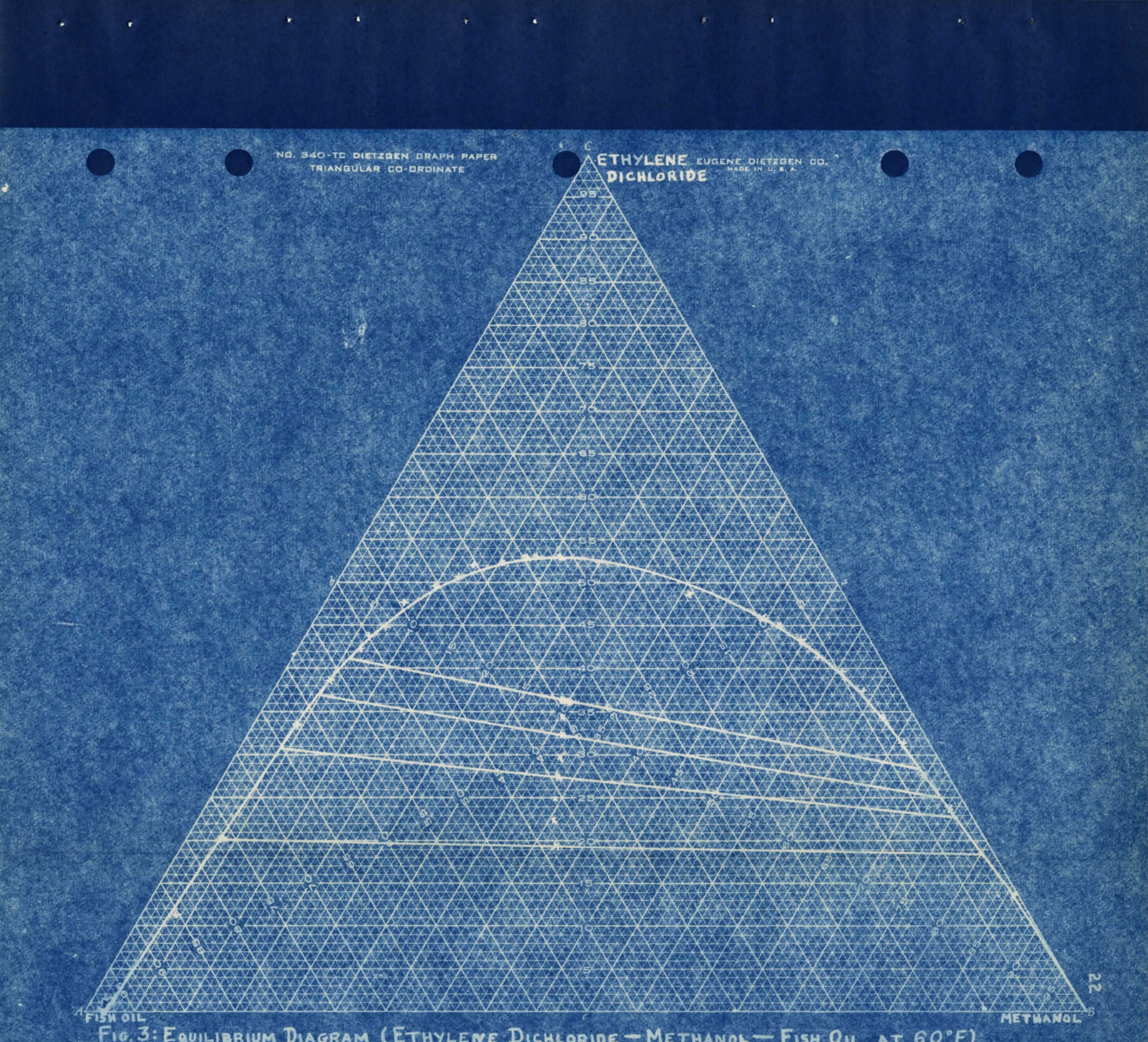

FIG. 3: EQUILIBRIUM DIAGRAM (ETHYLENE DICHLORIDE — METHANOL — FISH OIL AT 60°F)

ethane per milliliter confirmed the theory that the presence of nitroethane depresses the iodine value. The results of this test are shown in Table I.

n-Hexane is miscible with both fish oil and methanol. Before too much work was done on this system, an equilibrium diagram was determined, at 60°F, for the system methanol-n-hexane-fish oil. The results, Table IV and Fig. 4, showed that no appreciable extraction could be made with this system at room temperature.

At reduced temperatures, fish oil is only partially miscible with n-hexane, the degree of miscibility decreasing as the temperature is reduced.

Twenty-five milliliters of fish oil, at a temperature of 6°C, were extracted with a mixed solvent consisting of twenty-five milliliters of methanol dissolved in thirty milliliters of n-hexane. The extract layer contains the more unsaturated fraction of triglycerides. The extract was clear and of good odor, but the iodine number was not improved even after vacuum distillation and passage through the falling film evaporator.

Since traces of solvent depress the iodine number considerably, it was suspected that the iodine value might not show the true drying properties of the sample. A drying test was run on a sample of fish oil, extracted and treated as in the previous paragraph. This test was compared with the results of a drying test on raw oil. The drying rates of both

TABLE IV: EQUILIBRIUM DATA ON METHANOL-N-HEXANE-FISH OIL SYSTEM

Titration of Methanol into Oil / n-Hexane

ml Oil	ml n-Hexane	ml Methanol	Wt.Oil	Wt.n-Hexane	wt.Methanol	% Oil	%n-Hexane	%Methanol
20	0	0.1	18.560	0.0	0.07895	99.58	-----	0.42
20	6	0.3	18.560	3.9912	0.2368	81.45	17.51	1.03
20	10	0.35	18.560	6.6520	0.2763	72.82	26.10	1.08
20	12	0.4	18.560	7.9824	0.3158	69.10	29.72	1.18
20	16	0.5	18.560	10.6432	0.3948	62.71	35.96	1.33
20	18	0.6	18.560	11.9736	0.4737	59.86	38.62	1.53
20	20	0.7	18.560	13.3040	0.5526	57.26	41.04	1.70
20	22	0.75	18.560	14.6344	0.5921	54.93	43.31	1.75
20	24	0.8	18.560	15.9648	0.6316	52.79	45.41	1.80
20	26	0.9	18.560	17.2952	0.7106	50.76	47.30	1.94
20	28	1.0	18.560	18.6256	0.7895	48.87	49.05	2.08
20	30	1.1	18.560	19.9560	0.8684	47.13	50.67	2.20
20	32	1.3	18.560	21.2864	1.0264	45.41	52.08	2.51
20	34	1.5	18.560	22.6168	1.1842	43.81	53.39	2.80
20	36	1.8	18.560	23.9472	1.4211	42.26	54.51	3.24
20	38	2.0	18.560	25.2776	1.5790	40.87	55.66	3.48
20	40	---	------	-------	------	-----	-----	----
4	20	0.5	3.712	13.3040	0.3948	21.32	76.41	2.27
4	30	0.8	3.712	19.9560	0.6316	15.28	82.12	2.60
4	40	0.95	3.712	26.6080	0.7500	11.95	85.64	2.41

Titration of Oil into Methanol / n-Hexane

0.05	8	20	0.0464	5.3216	15.790	00.22	25.16	74.63
0.1	10	20	0.0928	6.6520	15.790	00.41	29.52	70.07
----	12	20	------	------	------	-----	-----	-----

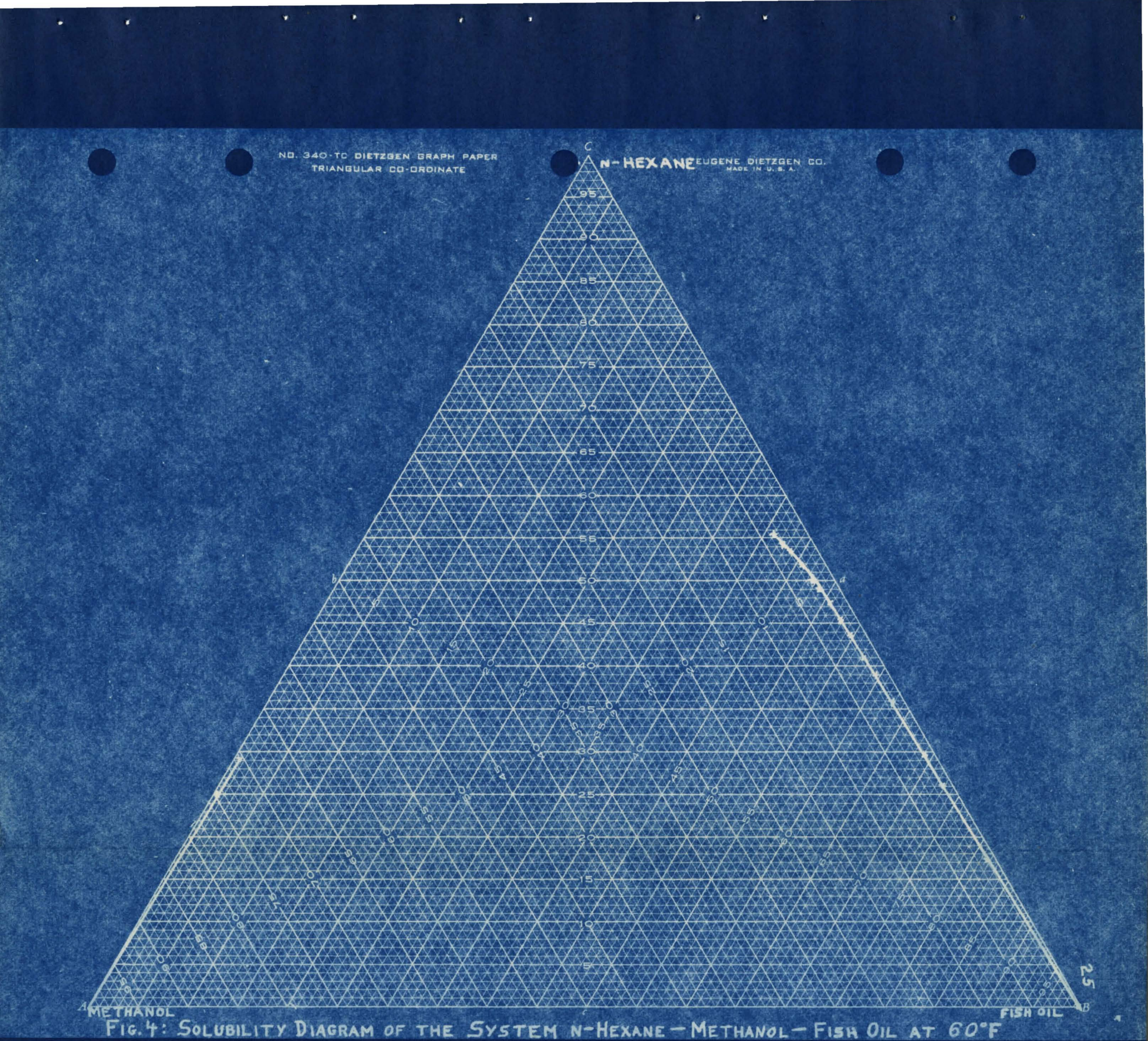

FIG. 4: SOLUBILITY DIAGRAM OF THE SYSTEM n-HEXANE — METHANOL — FISH OIL AT 60°F

the sample and the raw oil were so slow that cobalt naphthenate was added to the samples, and the tests rerun. The extracted sample dried to a tack free surface in three days against six days for the raw oil.

The drying test was checked and the results of the two tests are given in Table V and Fig. 5. The data show that the drying properties of the fish oil are improved by the extraction process. More improvement must be made in the drying properties of extracted menhaden oil before it can be classified as a "drying oil". An interesting feature of the drying data is that the initial rate of oxidation of the extracted oil is less than that of the raw oil. This condition is soon reversed. These results conform the theory that residual traces of solvent adversely affect the drying properties.

TABLE V: DATA ON DRYING TEST

Sample (extracted)	1 A 0.2024 gm.		2 A 0.2928 gm.	
time in hrs.	gain in wt.	% gain	gain in wt.	% gain
0.5	0.0014	0.692	0.0018	0.615
1.0	0.0058	2.866	0.0084	2.869
1.5	0.0084	4.150	0.0130	4.300
2.0	0.0088	4.348	0.0148	5.055
2.5	0.0118	5.830		
3.0	0.0126	6.225		
4.5			0.0226	7.719
5.5			0.0236	8.060

Sample (raw oil)	1 B 0.1976 gm.		2 B 0.3774 gm.	
time in hrs.	gain in wt.	% gain	gain in wt.	% gain
0.5			0.0028	0.742
1.0	0.0046	2.328	0.0082	2.173
1.5	0.0062	3.138	0.0124	3.286
2.0	0.0091	4.605		
3.0	0.0112	5.668		
4.0	0.0136	6.883	0.0250	6.624
4.5	0.0135	6.832	0.0264	6.995
5.0	0.0147	7.439	0.0270	7.154

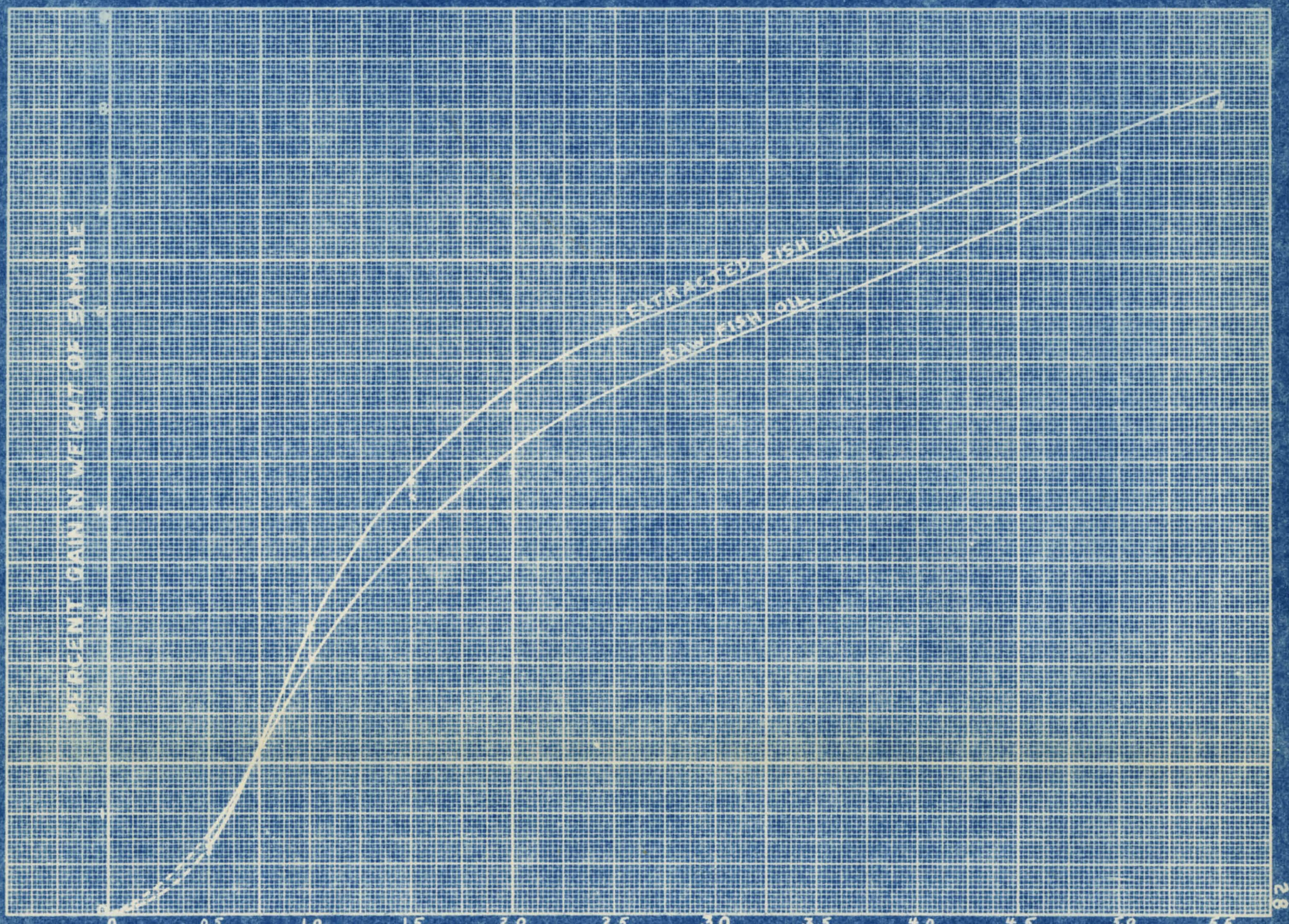

FIG. 5: DRYING TEST ON FISH OIL EXTRACTED AT 6°C WITH METHANOL—N-HEXANE

DISCUSSION

Much work has been done on extraction of saturated components of vegetable oils to improve drying properties. Since many of the same fatty acids are to be found in fish oil, it is to be expected that similar techniques might be applied to the oil of "Brevoortia tyrannus".

These experiments have proven the task of removing residual solvent without resorting to high temperatures to be very difficult. In fact, all traces of solvents were not removed at any time during the course of this work without polymerization occuring. This problem was to be expected although the degree of difficulty was not anticipated.

Some of the unsaturated fatty acids of fish oil are very highly unsaturated. Therefore, they are very sensitive to oxidation and, also, to polymerization. By maintaining a vacuum upon the system during distillation, the tendency toward oxidation was retarded. However since polymerization consists of the combination of unsaturated compounds by primary chemical linkages to form larger molecules of a saturated or less unsaturated type, the absence of oxygen or the reduction of its concentration in the atmosphere would not inhibit polymerization to any appreciable extent. One of the major variables affecting the tendency of a material to polymerize is temperature. It is obvious that excessive temperatures would induce polymerization of fish oil.

The mechanism of oil drying consists not only of oxidation. The oil presumably absorbs oxygen from the air. The unsaturated

fatty acid radicals are oxidized at some of the double bonds. These oxidized molecules readily polymerize to form larger molecular aggregates, and a micellar structure of practically solid polymers is formed. Cobalt naphthenate, when added to a drying oil, is primarily an oxidation catalyst. The gain in weight of the samples used in the drying tests does not show the complete picture of the drying procedure. But this discussion of "drying" shows that the results of the drying tests may be used to compare the drying properties of oils. The initial lag which occurred in the drying curve of the extracted oil can be attributed to evaporation of residual solvent from the plate.

The water present in commercial 190° proof alcohol and the cost of absolute alcohol prevented ethyl alcohol from being considered as a solvent. Other potential solvents were dismissed because of economic considerations. Acetonitrile, ethyl lactate, and methyl formate were in this group.

The results of these experiments indicate that low temperature extractions would be successful. Low temperature solvent extraction, followed by vacuum distillation of the extract, shows promise. The extract may be separated from the raffinate by utilization of a siphon, decantation, or, in some cases, filtration from a semi-solid mass.

SUMMARY AND CONCLUSIONS

It was possible to reduce the residual solvent content in both vacuum distilled extracts and raffinates by passing the samples through a falling film evaporator. Sufficient solvent could be removed, in most cases, to make it difficult to discover the presence of solvent by organoleptic methods. Some polymerization of the oil occurs during solvent removal. Some solvents depress iodine numbers of oils, even if the solvent is present in minute quantities.

An average iodine number of 196.3 was obtained on the extract of the system fish oil-ethylene dichloride-methanol. Drying tests on oil extracted with methanol-n-hexane, at reduced temperature, showed some improvement in drying properties.

Equilibrium data were not obtained on the system methanol-n-hexane-fish oil at 6 °C, the temperature of the extraction on which the drying tests were run, because of the limited solubility of fish oil in n-hexane. This limited solubility of fish oil makes the simplifying assumption, of fish oil being a single component, impossible to use. The saturated and unsaturated triglycerides must be considered as separate components in the system. Since the extraction system cannot be considered as a ternary system, conventional methods of correlation are useless. No successful method of correlation was discovered.

These experiments show that ethylene dichloride and n-hexane are promising components of solvent systems for fish

oil extraction. Reduced temperatures are desirable, and in the case of n-hexane, necessary for successful operation.

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APPENDIX

SOLUTIONS

(1) Hanus Solution (Iodine monobromide)

1. Dissolve 13.615 gms. of CP iodine crystals in 825 ml. of glacial acetic acid. The acid must be heated and stirred to make the iodine dissolve.
2. Cool iodine solution, pipet out 25 ml., and dilute to about 200 ml. with water.
3. Titrate with 0.1 N sodium thiosulfate solution.
4. Add 3 ml. of CP bromine to 200 ml. of glacial acetic acid.
5. Mix well, pipet out 5 ml., dilute to about 150 ml. with water, and add 10 ml. of 10% KI solution.
6. Titrate with 0.1 N sodium thiosulfate solution. (This titration should be about 80% of the iodine titration.)
7. Calculate the amount of bromine solution to add to the iodine solution as follows:

$$800 \times \frac{\frac{\text{titration of iodine solution}}{25}}{\frac{\text{titration of bromine solution}}{5}} = \text{ml. of bromine solution to be used}$$

8. Mix well, make up to 1 liter with acetic acid, and store in an amber glass-stoppered bottle.

(2) Sodium Thiosulfate (0.1 N solution)

1. Dissolve 24.82 gm. of $Na_2S_2O_3.5\ H_2O$ in CO_2 free distilled H_2O.
2. Dilute to 1 liter and add 0.1 gm. of Na_2CO_3 as a preservative.
3. Standardize against standard $K_2Cr_2O_7$ solution and calculate normality as follows:

$$\frac{(\text{Ml. of } K_2Cr_2O_7)(\text{normality})}{\text{Ml. of } Na_2S_2O_3} = \text{normality}$$

This solution deteriorates on standing and should be standardized about every two weeks.

(3) Potassium Dichromate (0.1 N solution)

1. Dissolve exactly 4.9037 gms. of $K_2Cr_2O_7$ in CO_2 free distilled H_2O.
2. Dilute to exactly one liter.

This solution is very stable and may be used as a primary standard.

(4) Starch Indicator

1. Make a paste of 2.5 gms. of soluble starch with water.
2. Add paste, with stirring, to one liter of boiling water, so slowly that boiling does not cease.
3. Add about one ml. of chloroform or toluene as a preservative.

(5) Potassium Iodide Solution

1. Dissolve 16.6 gm. of KI in distilled water and make up to a liter.

CALCULATIONS

Calculations for Iodine Number

(Hanus Method)

(Ml of $Na_2S_2O_3$ required by blank -- Ml of $Na_2S_2O_3$ required by sample)

$$(\text{normality of } Na_2S_2O_3)\left(\frac{12.692}{\text{weight of sample}}\right) = \text{iodine value}$$

VITA

Alan T. Thomas was born May 15, 1921 in Louisville, Kentucky. His father's name is Moses A. Thomas. His mother's maiden name was Ruth Lacefield.

His family moved to Larue County when he was five years old. He attended school at Lyons, Kentucky for four years. They moved back to Louisville in time for him to enter the Louisville public schools, in the fifth grade. He graduated from Louisville Male High School in February 1939 and entered the University of Louisville in September 1939. He received the degree of B. Ch. E. from Speed Scientific School on March 1, 1943.

Since graduation, Alan Thomas has been employed at Brown-Forman Distillers Corporation. His fields of specialization are "Solvent Extraction" and "Fermentation and Microbiology".

His major work was done under Dr. R. C. Ernst, Dr. G. C. Williams, and Mr. Wilson Barnes.